



# Remarkable improvement of the turn-on characteristics of a $\text{Fe}_2\text{O}_3$ photoanode for photoelectrochemical water splitting with coating a FeCoW oxy-hydroxide gel

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## ABSTRACT

A FeCoW oxy-hydroxide gel coated  $\text{Fe}_2\text{O}_3$  film photoanode has been examined for photoelectrochemical (PEC) water oxidation reaction. The FeCoW coating acts as a hole storage layer, resulting in efficient hole extraction from  $\text{Fe}_2\text{O}_3$  for water oxidation. In addition, the surface state of FeCoW/ $\text{Fe}_2\text{O}_3$  shifts to higher position, thus allows for a lower turn-on voltage ( $V_{\text{on}}$ ) of the photocurrent. The composite anode exhibits an 84% increase of the photocurrent, at 1.23 V versus reversible hydrogen electrode (RHE), over the bare  $\text{Fe}_2\text{O}_3$  photoanode. The  $V_{\text{on}}$  is as low as 0.67 V vs. RHE. The applied bias photon-to-current efficiency of the composite is 2.7 times higher than that of the bare  $\text{Fe}_2\text{O}_3$ . Moreover, an extremely low bias photore-sponse of 0.45 V vs. RHE and a good stability are observed with the FeCoW/ $\text{Fe}_2\text{O}_3$  photoanode. Besides, with changing of the thickness of the FeCoW coating slurry, the PEC performance of the FeCoW/ $\text{Fe}_2\text{O}_3$  photoanode can be tuned.

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## 1. Introduction

Due to the increased concern of energy supply and environmental issues, photoelectrochemical (PEC) water splitting becomes a challenging research topic in the field of sustainable energy. A smart design of PEC cell has two major counterparts, i.e. the photoanode for water oxidation and the photocathode for water reduction. As a multi-electron transfer process, the water oxidation at the photoanode has been one of the major bottlenecks for the overall PEC efficiency [1]. Among the intensively explored photoanode materials, hematite ( $\text{Fe}_2\text{O}_3$ ) stands out with its broad light spectrum absorption, durability in water, and natural abundance [2]. With a suitable band-gap of 2.0–2.2 eV, its theoretical solar energy conversion efficiency was predicted in the range of 12.7–16.8% [3,4]. Nevertheless, due to the short hole-diffusion length (2–4 nm), and the sluggish water oxidation kinetics on the surface,  $\text{Fe}_2\text{O}_3$  suffers

from a low photo responsive current and a high turn-on voltage which limit the energy conversion efficiency [5].

One of the approaches to improve the  $\text{Fe}_2\text{O}_3$  anode efficiency is to incorporate an oxygen evolution reaction (OER) catalyst [6,7]. Many OER catalysts, e.g. group 8–10 metal oxides, hydroxides and phosphates, have shown promoting effects in the PEC performance of  $\text{Fe}_2\text{O}_3$  [8–12]. In general, an OER catalyst enhances the performance in two ways, viz., extracts holes from  $\text{Fe}_2\text{O}_3$  phase thus enhancing the photocurrent, and shifts the surface state to a higher position accordingly facilitating a lower turn-on voltage ( $V_{\text{on}}$ ) of the photocurrent. However, the catalysts tested are often not efficient on both sides. For instance,  $\text{IrO}_2$  is inefficient to draw holes from  $\text{Fe}_2\text{O}_3$  [9], while  $\text{Co}_3\text{O}_4$  shows very limited contribution to shift the  $V_{\text{on}}$  of the photocurrent [13]. Meanwhile, the stability and cost of the OER catalyst are also crucial factors. With meeting both the two requirements mentioned, cobalt-phosphate (Co-Pi) was regarded as one of the most promising cocatalysts for  $\text{Fe}_2\text{O}_3$  photoanode. A recently discovered FeCoW oxy-hydroxide gel OER catalyst exhibited an exceptionally low over-potential, i.e. 191 mV at  $10 \text{ mA cm}^{-2}$  in alkaline electrolyte, as well as a good stability [14].

Herein, we present a successful effort using the FeCoW oxy-hydroxide as a surface promoter of the  $\text{Fe}_2\text{O}_3$  photoanode in

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water splitting. The FeCoW OER catalyst acts as an efficient and stable promoter simultaneously increasing the photocurrent with capturing the holes and decreasing the  $V_{on}$  with raising the location of the surface state.

## 2. Experimental

### 2.1. Materials synthesis

The  $Fe_2O_3$  film grown on fluorine-doped tin oxide (FTO) substrate was synthesized through a hydrothermal procedure reported previously [15,16]. In detail, 0.09 M ferric chloride and 0.1 M of sodium nitrate were dissolved in 25 mL deionized water. After filtration, the solution at pH = 1.4 (adjusted by HCl) was transferred to a 50 mL Teflon-lined stainless steel autoclave. FTO glass was immersed upside-down in the autoclave and heated at 95 °C for 4 h. After growth, the obtained yellow film was calcined at 550 °C for 2 h and further annealed at 800 °C for 20 min. The  $Fe_2O_3$  electrode with active area of  $1 \times 1 \text{ cm}^2$  was prepared after cooling to room temperature.

The synthesis procedure of the FeCoW oxy-hydroxide gel catalyst is consistent with literature [14]. Typically, to form the FeCoW ink, 3 mg of FeCoW powder was dispersed in 1 mL mixture of water and ethanol (4:1, v/v), and then 80  $\mu\text{L}$  of Nafion solution (5 wt.% in water) was added. The suspension with estimated concentration of  $3 \text{ mg mL}^{-1}$  was ultrasonically treated for 2 h. The FeCoW/ $Fe_2O_3$  films were prepared by spin-coating with the FeCoW suspension onto the  $Fe_2O_3$  film at 3000 rpm for 30 s. The number of spin coating times was controlled for varying the thicknesses of the FeCoW layer. A number of FeCoW concentrations of the suspension (1, 3, 5 and  $10 \text{ mg mL}^{-1}$ ) were examined for different FeCoW loading amount with the same spin speed and time.

A  $Co_3O_4/Fe_2O_3$  sample was prepared via a hydrothermal process [17]. 0.40 mL of 25%  $NH_3 \cdot H_2O$  was added into 25.0 mL of 5 mM  $Co(CH_3COO)_2 \cdot 4H_2O$  ethanol solution under vigorous stirring. After stirring for 10 min, the obtained brown sol was transferred into a Teflon-lined autoclave reactor with  $Fe_2O_3$  photoanode inside and hydrothermally treated at 120 °C for 1 h. After cooled down to room temperature naturally, the obtained  $Co_3O_4/Fe_2O_3$  anode was then washed and dried.

The Co-Pi/ $Fe_2O_3$  sample was prepared with a photoassisted electrodeposition technique [18]. 0.5 mM  $Co(NO_3)_2$  was dissolved in a buffer of 0.1 M  $KH_2PO_4$  adjusting to pH 7 with 1 M NaOH as the electrolyte. The deposition was carried out at +0.2 V vs. Ag/AgCl for 5 min with simulated sunlight illumination ( $100 \text{ mW cm}^{-2}$ ).

The  $FeOOH/Fe_2O_3$  sample was prepared via a dip coating process, i.e., the  $Fe_2O_3$  anode was immersed in a 5 mM  $FeCl_2 \cdot 4H_2O$  aqueous solution at 40 °C for 10 min followed by washing and drying [19].

### 2.2. Photoelectrochemical measurements

The photocurrent was recorded with an electrochemical workstation (CHI 660B, CH Instrument, Chenhua, Shanghai) using a three-electrode configuration with Ag/AgCl as the reference electrode, Pt sheet ( $1 \times 1 \text{ cm}^2$ ) as the counter electrode and 1.0 M NaOH (70 mL, pH 13.6) as the electrolyte which is contained in a quartz reactor with a volume of 150 mL. The polarization curves were scanned at  $20 \text{ mV s}^{-1}$  under filtered AM 1.5G simulated sunlight from a 300 W xenon lamp (Perfect Light, PLS-SXE-300). The light intensity was measured as  $100 \text{ mW cm}^{-2}$  using a radiometer (Sanpometer SM206). If not otherwise specified, the anodes were illuminated from the back-side. Transient chronoamperometry was performed with sample interval of 0.001 s. EIS measurements under AM 1.5G illumination were carried out in a frequency from

100 kHz to 1 Hz with applying amplitude of 20 mV at different applied bias. All potentials were referenced to the reversible hydrogen electrode (RHE) with the Nernst equation [20]:

$$V_{RHE}(V) = V_{Ag/AgCl}(V) + 0.1976 + 0.059 \text{ pH}$$

The applied bias photo-to-current conversion efficiency (ABPE) was calculated by the following equation [21]:

$$ABPE = \frac{J \times (1.23 - |V_{RHE}|)}{P} \times 100\%$$

where  $J$  is the photocurrent density ( $\text{mA cm}^{-2}$ ) at the applied bias  $V$  vs. RHE, and  $P$  is the incident light intensity ( $\text{mW cm}^{-2}$ ).

The produced  $H_2$  and  $O_2$  were collected and measured. The reactor was previously purged with  $N_2$  for 30 min to eliminate the dissolved oxygen and the air in the reactor. After reaction at 1.23 V vs. RHE,  $H_2$  and  $O_2$  were carried out by continuous  $N_2$  flow ( $20 \text{ mL min}^{-1}$ ) and collected with a gas sampling bag. For each sampling with an interval of 30 min, 1 mL gas was pumped out with a chromatography needle and injected in the gas chromatograph (GC, Agilent 6890D, TCD detector, molecular sieve 5A column, carrier gas (Ar) flow rate of  $36 \text{ mL min}^{-1}$ , oven temperature of 50 °C and detector temperature of 120 °C). The amounts of  $H_2$  and  $O_2$  were calculated with  $N_2$  as a reference.

### 2.3. Characterization

The X-ray diffraction patterns (XRD) were collected from 20° to 70° at a speed of  $8^\circ \text{ min}^{-1}$  with a Bruker AXS, D8-S4 powder diffractometer with Cu K $\alpha$  illumination (40 kV  $\times$  200 mA). The SEM images were recorded using a Hitachi S-4800 field emission scanning electron microscope. The TEM and high-resolution TEM micrographs were examined by a transmission electron microscope (TEM, JEM-2100F). The UV-visible (UV-vis) diffuse reflection characteristic was obtained with the diffuse reflection method on a Perkinelmer L750 spectrometer. The X-ray photoelectron spectroscopy (XPS) measurement was detected with an ESCA PHI 1600 instrument using an Mg K $\alpha$  X-ray source for excitation. The C 1s binding energy at 284.6 eV is used for spectrum calibration.

## 3. Results and discussion

### 3.1. Material characterization

The FeCoW suspension was synthesized via a sol-gel technique. The elemental mapping results in Fig. 1 confirm a uniform distribution of Fe, Co, W and O elements in the dried FeCoW powder. As indicated from the XRD patterns in Fig. 2, the samples exhibit a typical crystal structure of  $\alpha\text{-Fe}_2\text{O}_3$  (JCPDS No. 33-0664) with an oriented growth of (110) plane. The FeCoW coating showed no impact on the crystal structure or the crystallinity of  $Fe_2O_3$ . The morphologies of the photoanode materials recorded with SEM and TEM images are illustrated in Fig. 3. The  $FeOOH$  sample, shown in the insert of Fig. 3a, displays a porous surface. After annealing at 800 °C, the  $Fe_2O_3$  film show slight sintering with higher porosity (Fig. 3a). After coating of the FeCoW gel via a spin-coating technique, the surface of the  $Fe_2O_3$  film becomes rough, as shown in Fig. 3b. The FeCoW/ $Fe_2O_3$  composite displays a uniform morphology in the low magnification image in Fig. 3c. A full coverage of a FeCoW layer on  $Fe_2O_3$  is confirmed by the TEM image (Fig. 3f). As observed in the HRTEM micrograph, a thin disorder layer is seen on the bare  $Fe_2O_3$  (Fig. 3d), while a much thicker amorphous layer of FeCoW is observed on the surface of FeCoW/ $Fe_2O_3$  (Fig. 3e). The thickness of the FeCoW overlayer is measured to be about 2 nm by subtracting the thickness of the disorder layer.

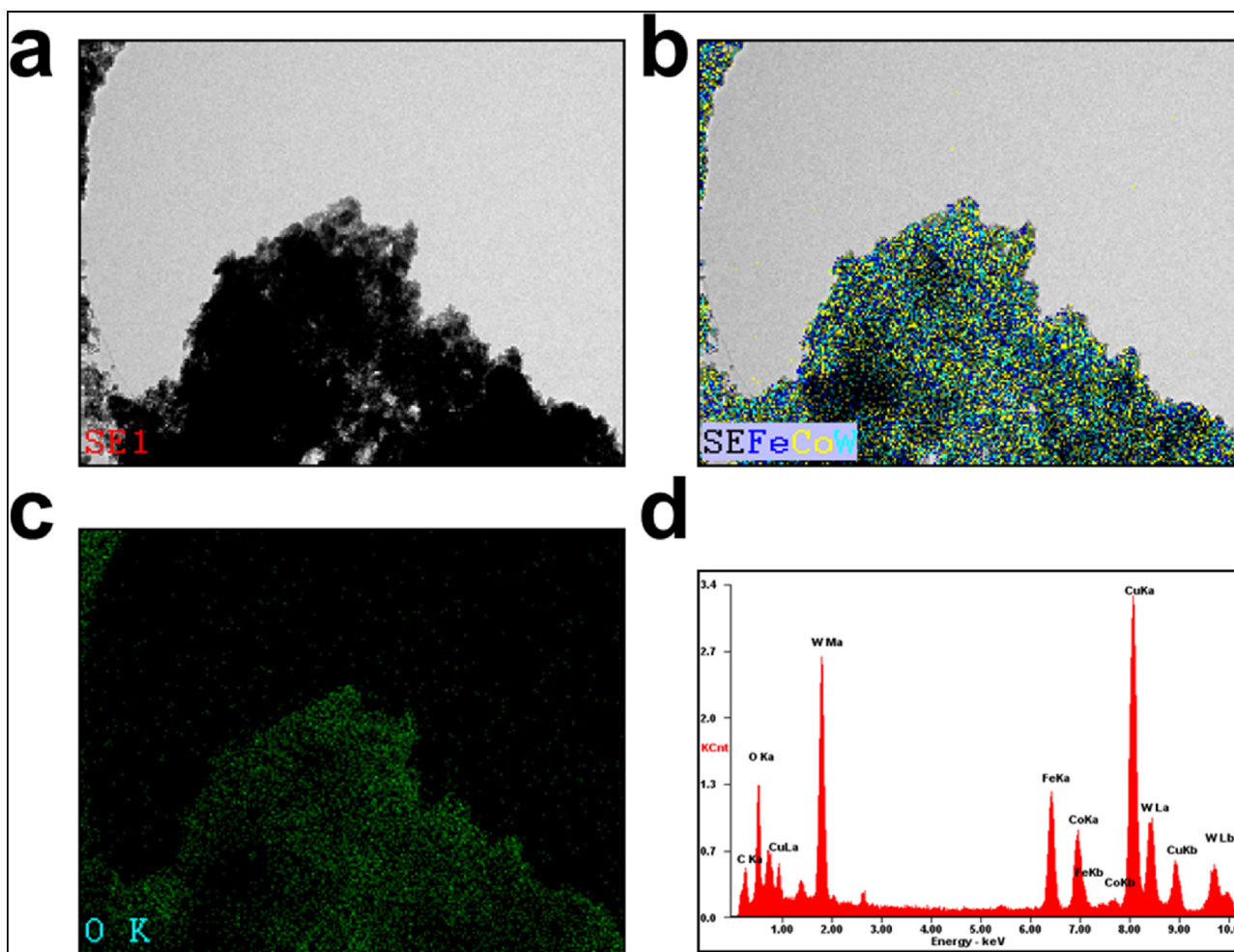


Fig. 1. (a) TEM micrograph of the FeCoW sample, EDX mapping of (b) the mixed Fe, Co and W elements, (c) O element and (d) EDX element distribution of the FeCoW powder.

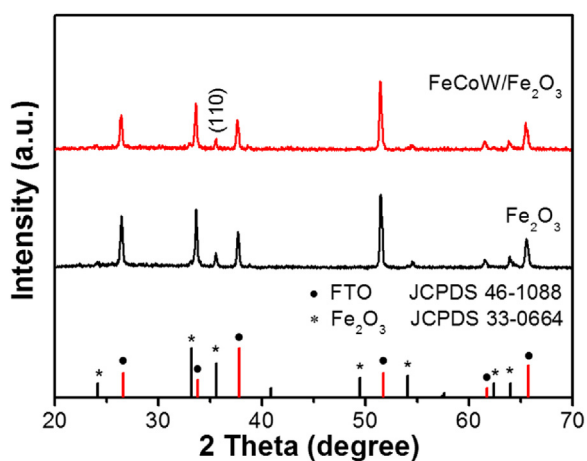


Fig. 2. XRD patterns of the Fe<sub>2</sub>O<sub>3</sub> and FeCoW/Fe<sub>2</sub>O<sub>3</sub> samples.

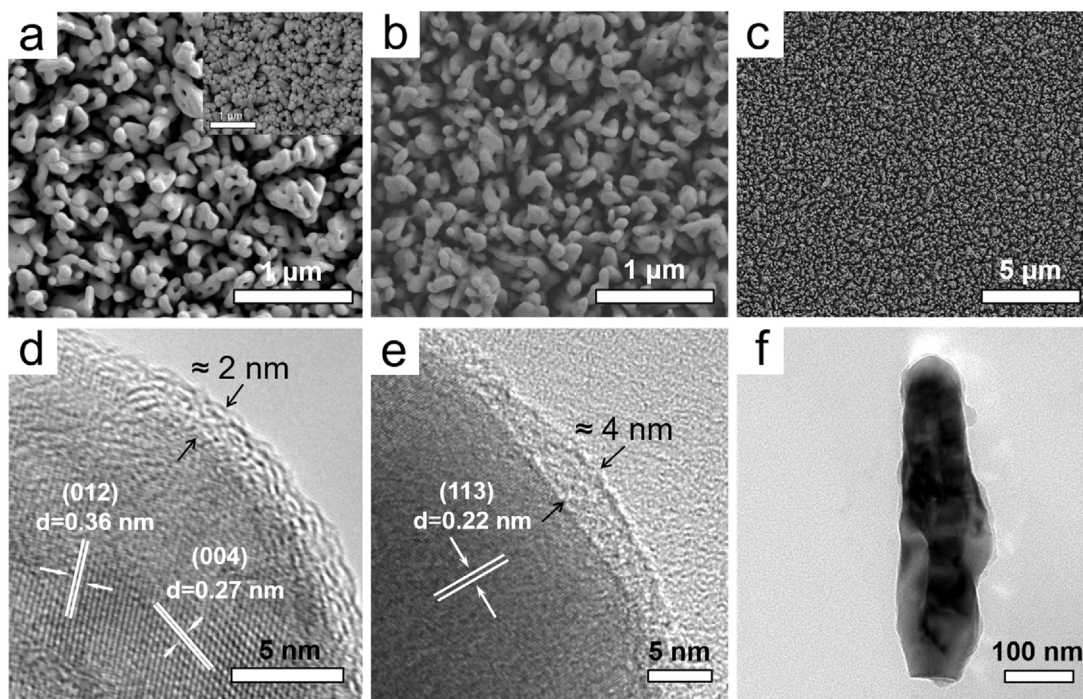
The XPS spectra of the O 1s region were obtained from vacuum dried Fe<sub>2</sub>O<sub>3</sub> and FeCoW/Fe<sub>2</sub>O<sub>3</sub> surfaces, as depicted in Fig. 4a. The O 1s spectrum of Fe<sub>2</sub>O<sub>3</sub> shows as convoluted double peaks which are assigned to the lattice and hydroxyl oxygen, respectively [22]. Notably, the binding energy of the lattice oxygen in FeCoW/Fe<sub>2</sub>O<sub>3</sub> broadens and shows a 0.9 eV shift to the higher end from that of Fe<sub>2</sub>O<sub>3</sub>, and becomes higher than that of the Co–O, but still lower than that of the W=O bond [23,24], which is due to the coexistence

of lattice oxygen bonding with the three metal atoms. In addition, the much stronger hydroxyl O 1s peak in FeCoW/Fe<sub>2</sub>O<sub>3</sub> is attributed to the hydroxylated surface of the FeCoW layer. Besides, the additional peak at 535.8 eV is speculated to be the oxygen in the ether configuration brought from Nafion solution [25]. The UV–vis diffuse reflection spectra of the Fe<sub>2</sub>O<sub>3</sub>, FeCo/Fe<sub>2</sub>O<sub>3</sub> and FeCoW/Fe<sub>2</sub>O<sub>3</sub> samples are given in Fig. 4b. The difference of the UV–vis absorption characteristic between the bare and the composite samples is very slight, indicating no additional photoresponse induced by the coating of a FeCo or FeCoW layer.

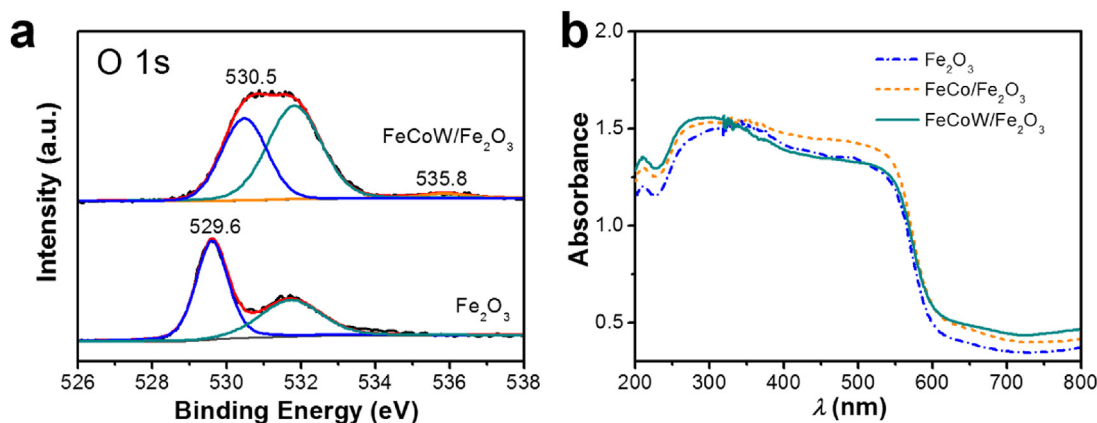
### 3.2. Photoelectrochemical performance

The promotion effect of the FeCoW layer on the Fe<sub>2</sub>O<sub>3</sub> photoanode is examined by measuring the polarization curve at a scan rate of 20 mV s<sup>−1</sup> under standard simulated AM 1.5 G irradiation in 1 M NaOH electrolyte, as given in Fig. 5a. A reference sample FeCo oxy-hydroxide coated Fe<sub>2</sub>O<sub>3</sub>, which was synthesized similarly as the FeCoW/Fe<sub>2</sub>O<sub>3</sub> is also measured. The turn-on voltages are derived with a Butler plot, shown as Fig. 5b, where the V<sub>on</sub> shifted to cathode side by 100 mV (from 0.84 V to 0.74 V) and by 170 mV (from 0.84 V to 0.67 V) for the FeCo and FeCoW coated samples, respectively. Likewise, the photocurrent density shows a substantial increase from 0.64 to 1.04 and further to 1.18 mA cm<sup>−2</sup> at 1.23 vs. RHE. The applied bias photon-to-current efficiency (ABPE) is calculated with the data derived from the polarization curve with assuming a 100% Faradaic efficiency (Fig. 5c). The maxi-





**Fig. 3.** (a) SEM images of  $\text{Fe}_2\text{O}_3$ , insert is the SEM image of the  $\text{FeOOH}$  sample; (b, c)  $\text{FeCoW}/\text{Fe}_2\text{O}_3$  photoanodes. HRTEM images of (d) bare  $\text{Fe}_2\text{O}_3$  and (e)  $\text{FeCoW}/\text{Fe}_2\text{O}_3$  surface. (f) TEM image of a  $\text{FeCoW}/\text{Fe}_2\text{O}_3$  nanowire.



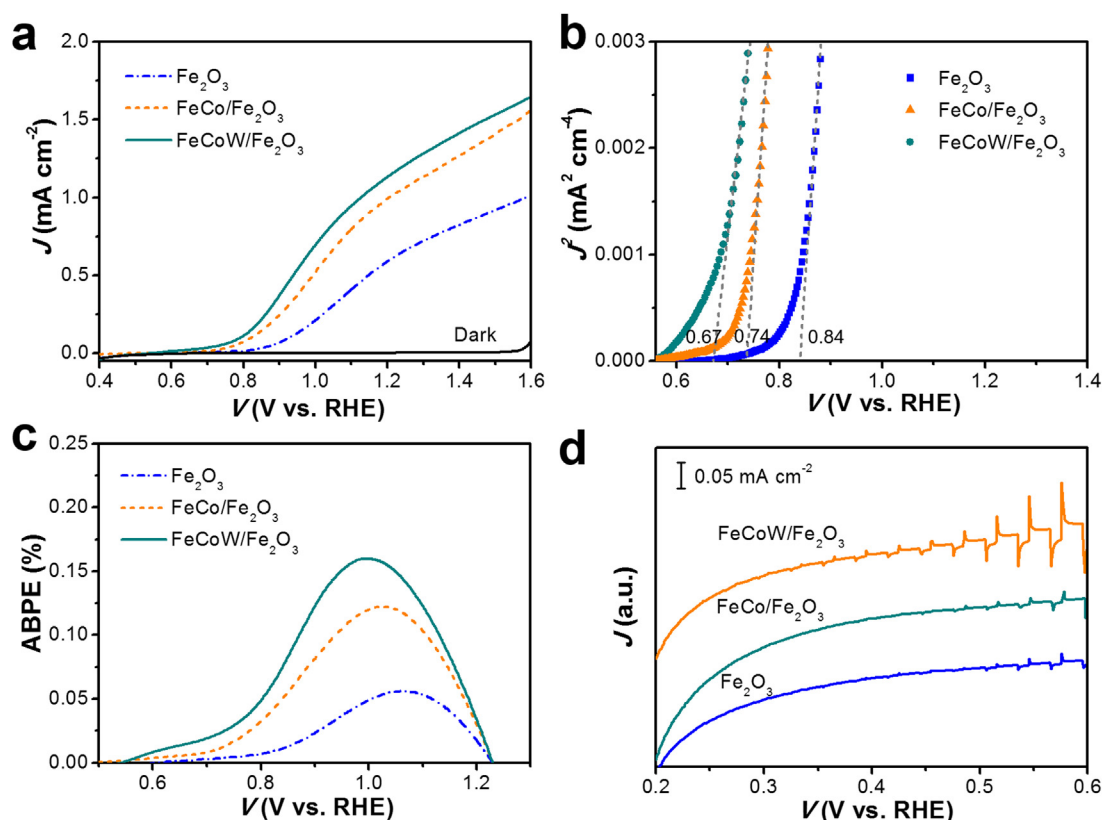
**Fig. 4.** (a) High-resolution XPS spectra of the O 1s region from vacuum dried  $\text{Fe}_2\text{O}_3$  and  $\text{FeCoW}/\text{Fe}_2\text{O}_3$  surfaces. (b) UV-vis diffuse reflection spectra of the  $\text{Fe}_2\text{O}_3$ ,  $\text{FeCo}/\text{Fe}_2\text{O}_3$  and  $\text{FeCoW}/\text{Fe}_2\text{O}_3$  samples.

imum ABPE of the  $\text{FeCo}/\text{Fe}_2\text{O}_3$  anode achieves 0.12%, which is twice of that of the non-promoted  $\text{Fe}_2\text{O}_3$  of 0.06%. The  $\text{FeCoW}/\text{Fe}_2\text{O}_3$  anode gives a further enhanced maximum ABPE of 0.16%, meanwhile, the voltage at the maximum ABPE also shifts to cathode side by 0.07 V. Further low voltage was applied to the photoanode (Fig. 5d) and a significant photoresponse is observed at around 0.45 V for the  $\text{FeCoW}/\text{Fe}_2\text{O}_3$  sample, which is impressive, since the theoretically necessary bias is 0.3–0.4 V for  $\text{Fe}_2\text{O}_3$  to initiate the water splitting reaction [26]. In contrast,  $\text{FeCo}$  does not show an obvious improvement of the low bias performance.

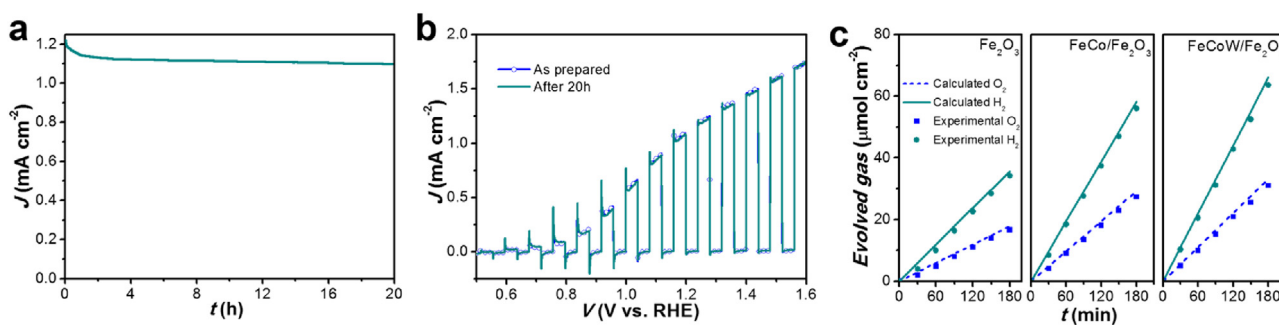
Long-term photocurrent density under continuous illumination was measured to test the photostability of the  $\text{FeCoW}/\text{Fe}_2\text{O}_3$  photoanode, as given in Fig. 6a. A slight decay during 20 h of photoelectrolysis run at 1.23 V vs. RHE was observed. After the renewal of the electrolyte, the PEC performance shows a complete recovery (Fig. 6b). The outstanding stability is attributed to the strong adhesion of the superbly stable  $\text{FeCoW}$  catalyst on  $\text{Fe}_2\text{O}_3$  in the alkaline solution.

The  $\text{H}_2$  and  $\text{O}_2$  gases generated in 3 h from the  $\text{Fe}_2\text{O}_3$ ,  $\text{FeCo}/\text{Fe}_2\text{O}_3$  and  $\text{FeCoW}/\text{Fe}_2\text{O}_3$  photoanodes were collected and quantified (Fig. 6c). For all the samples, the ratio of evolved  $\text{O}_2$  and  $\text{H}_2$  is around 2.1. The slight discrepancy with stoichiometry is probably due to the inevitable  $\text{O}_2$  dissolution. The  $\text{H}_2$  and  $\text{O}_2$  evolution amounts were increased with  $\text{FeCo}$  coating and further enhanced by  $\text{FeCoW}$  coating, which is consistent with the photocurrent results. The Faraday efficiency of the  $\text{O}_2$  evolution reaction for the samples is identical and is determined to be 90–94% after the system reaches a steady state. Thus, the photogenerated holes were utilized for  $\text{O}_2$  production in the system.

A number of  $\text{FeCoW}/\text{Fe}_2\text{O}_3$  samples with changing the thickness of the  $\text{FeCoW}$  coating slurry and the number of coatings were prepared and examined. The polarization curves are presented in Fig. 7. Substantially, the increase of the  $\text{FeCoW}$  gel thickness corresponds to an increased photocurrent but the turn-on voltages are almost the same. However, increase of the  $\text{FeCoW}$  coating layers leads to a negative effect on both the photocurrent value and



**Fig. 5.** (a) Respective polarization curves, (b) Butler plots, (c) Applied bias photon-to-current conversion efficiency (ABPE) and (d) Low-bias polarization curves for the  $\text{Fe}_2\text{O}_3$ ,  $\text{FeCo}/\text{Fe}_2\text{O}_3$  and  $\text{FeCoW}/\text{Fe}_2\text{O}_3$  photoanodes. The turn-on voltage is derived from the Butler plots as the value at which the extrapolation of the linear relationship between  $J^2$  and  $V$  intercepts with  $J^2 = 0$ .



**Fig. 6.** (a) Long-term chronoamperometry of the  $\text{FeCoW}/\text{Fe}_2\text{O}_3$  photoanode at 1.23 V vs. RHE, (b) Polarization curves of the as prepared and long-term tested  $\text{FeCoW}/\text{Fe}_2\text{O}_3$  photoanode in fresh electrolyte, (c) Evolution of  $\text{H}_2$  and  $\text{O}_2$  gases from the  $\text{Fe}_2\text{O}_3$ ,  $\text{FeCo}/\text{Fe}_2\text{O}_3$  and  $\text{FeCoW}/\text{Fe}_2\text{O}_3$  photoanodes at 1.23 V vs. RHE with comparison to the gas evolutions estimated from the current generation.

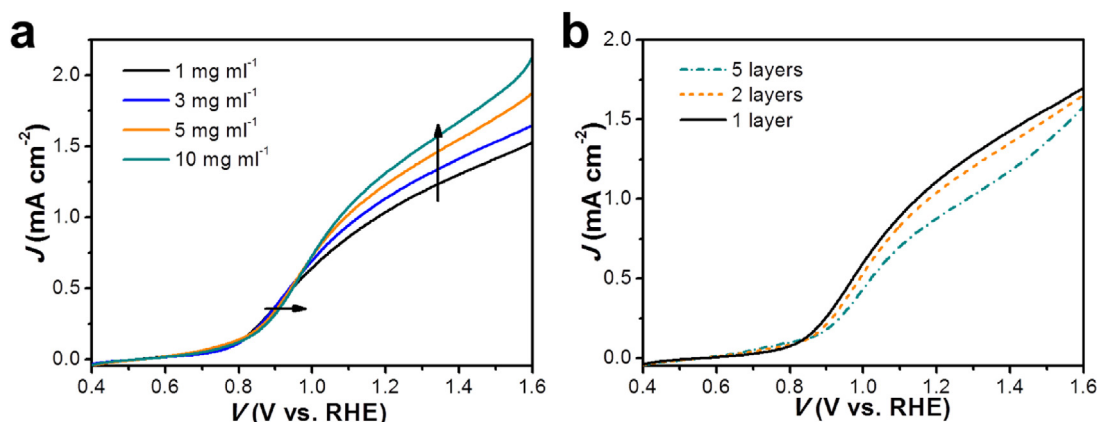
the turn-on voltage. These results suggest that thin layer coating of  $\text{FeCoW}$  effectively promotes the PEC performance of  $\text{Fe}_2\text{O}_3$  and with the increase of the thickness of the  $\text{FeCoW}$  coating slurry, the promotion effect is enhanced in a range.

A number of OER catalysts, i.e.,  $\text{FeOOH}$ ,  $\text{Co}_3\text{O}_4$  and  $\text{Co-Pi}$ , loaded  $\text{Fe}_2\text{O}_3$  samples, those showed good PEC performance and photostability in recent reports, were also prepared as references. The comparison of the polarization curves for the samples is presented in Fig. 8. The OER catalysts show different promotion effects on the photocurrent response of  $\text{Fe}_2\text{O}_3$ . Regardless of the bare  $\text{Fe}_2\text{O}_3$ , the  $\text{FeOOH}/\text{Fe}_2\text{O}_3$  anode shows the lowest photocurrent among them. The  $\text{Co}_3\text{O}_4/\text{Fe}_2\text{O}_3$  anode exhibits a similar performance with  $\text{FeCo}/\text{Fe}_2\text{O}_3$ . Particularly, the turn-on voltage of  $\text{FeCoW}/\text{Fe}_2\text{O}_3$  anode is as low as the well-known  $\text{Co-Pi}/\text{Fe}_2\text{O}_3$ . Most significantly,

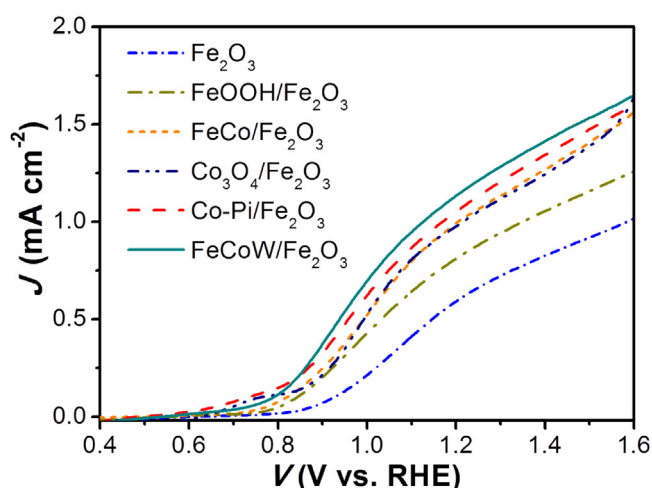
the  $\text{FeCoW}/\text{Fe}_2\text{O}_3$  anode shows even higher photocurrent than that of  $\text{Co-Pi}/\text{Fe}_2\text{O}_3$  when the bias is above 0.85 V.

### 3.3. Photoelectrochemical characterization

The electrochemical impedance spectra (EIS) of the electrode samples under AM 1.5G illumination were also measured. The equivalent circuit (EC) for interpreting the EIS data is proposed and illustrated in Fig. 9a, which consists of a couple of capacitances and resistances in parallel [27,28]. The representative Nyquist plots at 1.0V under illumination are presented in Fig. 9b. Each curve composes two semicircles. The semicircle at high frequency is related to the charge transfer resistance in the bulk, and the one at low frequency ascribes to the charge transfer resistance at the



**Fig. 7.** Polarization curves of the FeCoW/Fe<sub>2</sub>O<sub>3</sub> photoanodes prepared with spin-coating with (a) changed FeCoW suspension concentrations at a spin-coating speed of 3000 rpm and (b) changed spin-coating times at a speed of 3000 rpm with 3 mg ml<sup>-1</sup> FeCoW suspension.

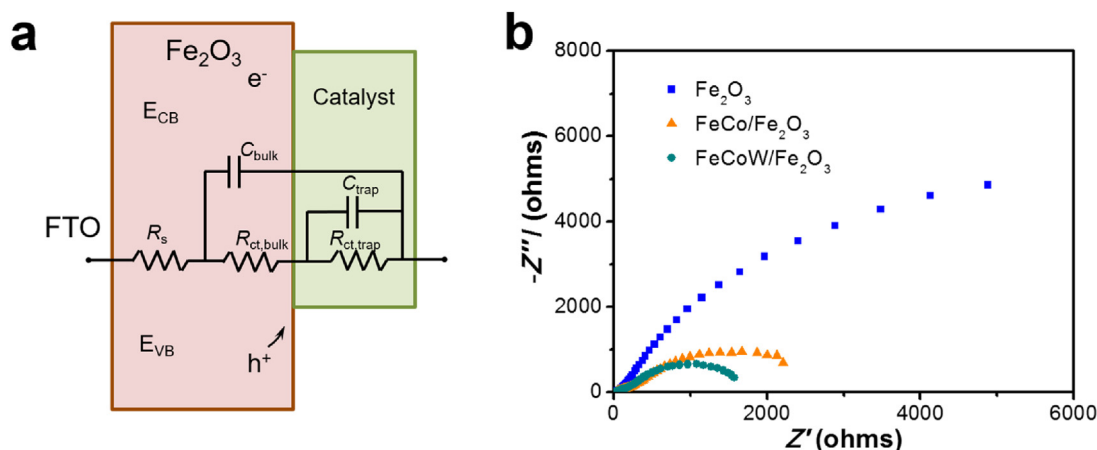


**Fig. 8.** Comparison of the polarization curves of the Fe<sub>2</sub>O<sub>3</sub>, FeOOH/Fe<sub>2</sub>O<sub>3</sub>, FeCo/Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>/Fe<sub>2</sub>O<sub>3</sub>, Co-Pi/Fe<sub>2</sub>O<sub>3</sub> and FeCoW/Fe<sub>2</sub>O<sub>3</sub> photoanode samples.

anode/electrolyte interface [29]. The diameter of the second semi-circle of the FeCoW/Fe<sub>2</sub>O<sub>3</sub> sample is smaller than that of FeCo/Fe<sub>2</sub>O<sub>3</sub> and much smaller than that of the Fe<sub>2</sub>O<sub>3</sub>. The values of  $R_{ct,bulk}$  of the FeCo/Fe<sub>2</sub>O<sub>3</sub> and FeCoW/Fe<sub>2</sub>O<sub>3</sub> anodes are quite similar to each other and are both small, in the order of  $10^2$ – $10^3 \Omega \text{ cm}^2$  (Fig. 10a), indicating the fast hole transfer from the valence band (VB) of Fe<sub>2</sub>O<sub>3</sub>

to the coating layers. Klahr et al. [30] examined the Co-Pi coated hematite with similar  $R_{ct,bulk}$  values and proposed these resistances are consistent with having fast charge transfer of holes from the VB of hematite to the Co-Pi. The values of the trap capacitance ( $C_{trap}$ ), and FeCoW shows a much profound effect than that of FeCo. The increase of the  $C_{trap}$  values means the improvement of the hole capture and storage capability of the anode material [31], suggesting that the FeCoW coating behaves as a hole storage layer to extract holes from Fe<sub>2</sub>O<sub>3</sub>. Meanwhile, the  $R_{ct,trap}$  value, reversely correlated to the rate of hole transfer from the solid surface to the adsorbed water molecule, decreases with the order uncoated, FeCo coated and FeCoW coated Fe<sub>2</sub>O<sub>3</sub> (Fig. 10c) for the three samples. The decrease of  $R_{ct,trap}$  indicates the decrease of the recombination ratio of the surface electron-hole pairs, thus resulting in the acceleration of the surface water oxidation reaction [9,32]. For the three samples, the  $V_{on}$  is correlated coincidentally with the peak location of the  $C_{trap}$ , indicating that the reaction is controlled predominantly by the hole transfer at the interface. As confirmed by the higher  $C_{trap}$  and lower  $R_{ct,trap}$  values, FeCoW exhibits a better catalytic effect than FeCo does.

The capturing effect of holes by FeCo and FeCoW catalysts is more intuitively reflected in the Bode plots of the anodes. The higher of the phase value reflects the more accumulation of charge at a certain interface [33]. The Bode plots of the Fe<sub>2</sub>O<sub>3</sub>, FeCo/Fe<sub>2</sub>O<sub>3</sub> and FeCoW/Fe<sub>2</sub>O<sub>3</sub> electrodes at three representative applied potentials are presented in Fig. 11. At 0.7 V all the examined electrodes



**Fig. 9.** (a) Equivalent circuit used for interpretation of the hematite electrodes loaded with an OER catalyst. (b) Nyquist plots of the Fe<sub>2</sub>O<sub>3</sub>, FeCo/Fe<sub>2</sub>O<sub>3</sub> and FeCoW/Fe<sub>2</sub>O<sub>3</sub> photoanodes under AM 1.5 illumination.

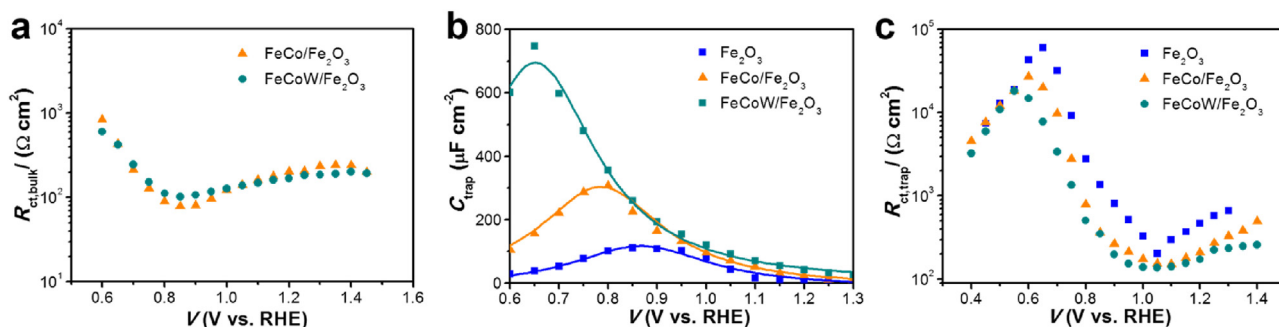


Fig. 10. (a)  $R_{ct,bulk}$ , (b)  $C_{trap}$  and (c)  $R_{ct,trap}$  fitting plots from EIS response of the  $Fe_2O_3$ ,  $FeCo/Fe_2O_3$  and  $FeCoW/Fe_2O_3$  photoanodes under AM 1.5 illumination.

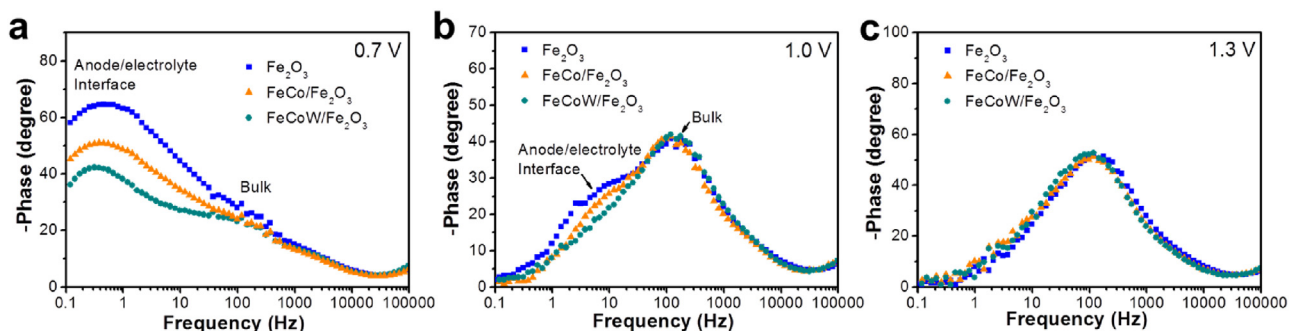


Fig. 11. Bode plots of the  $Fe_2O_3$ ,  $FeCo/Fe_2O_3$  and  $FeCoW/Fe_2O_3$  electrodes at (a) 0.7 V, (b) 1 V and (c) 1.3 V.

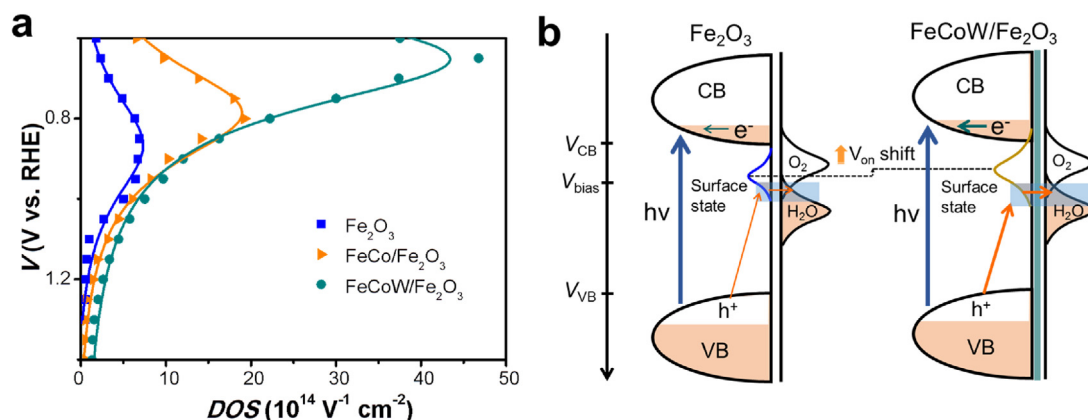


Fig. 12. (a) Applied voltage versus densities of surface states (DOS) of the electrodes. Solid lines correspond to Lorentzian fit results. (b) Proposed kinetic scheme of the hole transfer pathways from the VB of  $Fe_2O_3$  to the surface states for the  $Fe_2O_3$  and  $FeCoW/Fe_2O_3$  photoanodes under illumination at a bias of 1.0 V vs. RHE. Shaded and blank areas represent electron filled or empty states, respectively.

showed two characteristic peaks centered at around 0.4 and 170 Hz (Fig. 11a). The low frequency peak of the electrodes shows much higher phase value, suggesting that the water oxidation is limited by charge transfer at the anode/electrolyte interface at this potential. The low frequency peak of  $FeCoW/Fe_2O_3$  electrodes is much lower than that of bare  $Fe_2O_3$ , suggesting that part of holes trapped in the surface state is captured by the  $FeCoW$  layer for water oxidation. At 1.0 V in Fig. 11b, the high frequency peak of the bare  $Fe_2O_3$  becomes much larger and the low frequency peak is reduced, suggesting that at this potential the surface reaction was predominantly limited by bulk transfer of holes. By contrast, the low frequency peak of  $FeCoW/Fe_2O_3$  electrode almost disappeared, indicating the holes trapped in the surface state of  $Fe_2O_3$  are totally captured by the  $FeCoW$  layer. At 1.3 V in Fig. 11c, the low frequency peaks of the three electrodes all disappear, leaving only one peak visible. At this potential, which is higher than the thermo-

dynamic potential of water splitting (1.23 V), the water oxidation is only limited by the intrinsic properties of the  $Fe_2O_3$ , and thus the bare and promoted anodes reveal similar bode plots.

The density of surface state (DOS) is extracted from the  $C_{trap}$  plots ( $C_{trap} = q \times DOS$ , Fig. 12a) [34]. A kinetic scheme of the hole transfer pathways from the VB of  $Fe_2O_3$  to the surface states for the  $Fe_2O_3$  and  $FeCoW/Fe_2O_3$  photoanodes at 1.0 V vs. RHE is proposed, illustrated as Fig. 12b. For both photoanodes, the surface states locate inside the band-gap and the hole transfers from the top of the VB of  $Fe_2O_3$ . The  $V_{on}$  of the photocurrent occurs when half of the surface states are emptied, so that, for the  $FeCoW$  coated  $Fe_2O_3$ , the surface state locates energetically higher, allowing for a lower  $V_{on}$  of the photocurrent [27]. On the other hand, the hole transfer rate and the corresponding photocurrent depend on the overlapping (light blue shade) between the filled surface states and the filled redox couple states ( $H_2O$ ) [35]. Hence, at a certain polarization



voltage, the FeCoW/Fe<sub>2</sub>O<sub>3</sub> photoanode provides a higher available filled surface state and thus leads to an increased photocurrent.

#### 4. Conclusion

Here, we showed that a thin layer of FeCoW coating displays a profound promoting effect on the performance of a Fe<sub>2</sub>O<sub>3</sub> photoanode.

As evidenced from the EIS Bode and Nyquist plots, the FeCoW layer collects and stores the photogenerated holes from the Fe<sub>2</sub>O<sub>3</sub> electrode under illumination, thus accelerating charge separation and inhibiting surface recombination. FeCoW coating also shifts the surface state to higher location which allows for a lowered  $V_{on}$ .

The  $V_{on}$  is confirmed to shift to the cathode side by 170 mV and the photocurrent is increased by 84% at 1.23 V vs. RHE for the FeCoW coated sample over the bare Fe<sub>2</sub>O<sub>3</sub> photoanode. In addition, it is impressive that the FeCoW/Fe<sub>2</sub>O<sub>3</sub> composite photoanode achieves an extraordinarily low bias photoresponse at a voltage of 0.45 V. Furthermore, the composite photoanode exhibits an excellent stability during 20 h illumination. Moreover, with regulating the thickness of the FeCoW coating slurry, the promotion effect on the PEC performance of Fe<sub>2</sub>O<sub>3</sub> can be further tuned.

The promoting effect of the FeCoW oxyhydroxide gel on the turn-on characteristics and photocurrent performance of the Fe<sub>2</sub>O<sub>3</sub> photoanode is confirmed to be much stronger than that of FeOOH or Co<sub>3</sub>O<sub>4</sub> OER catalysts. The turn-on characteristics of the FeCoW/Fe<sub>2</sub>O<sub>3</sub> is comparable to that of the Co–Pi catalyst. Moreover, the photocurrent of the FeCoW/Fe<sub>2</sub>O<sub>3</sub> is slightly higher than that of the Co–Pi/Fe<sub>2</sub>O<sub>3</sub> photoanode.

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